

## Cu(hfa)<sub>2</sub>( $\mu$ -1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC)의 합성과 특성 분석

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## Synthesis and Characterization of Cu(hfa)<sub>2</sub>( $\mu$ -1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC)

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Crystal engineering and the design of solid-state architectures have become an area of increasing interest over recent years. The packing of molecules into arrays of beautiful structures is the result of metal-ligand interactions<sup>1-4</sup> or noncovalent interactions (hydrogen bonding,  $\pi$ - $\pi$  stacking, etc.).<sup>5-7</sup> With this in mind, we were interested in monitoring 1) the formation of multidimensional networks and 2) the effect of ligand bulk on the  $\pi$ - $\pi$  stacking interactions.<sup>8-10</sup> Herein, we describe the synthesis and characterization of two copper complexes, Cu(hfa)<sub>2</sub>( $\mu$ -1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC). The Cu(hfa)<sub>2</sub>( $\mu$ -1,4-dicyanobenzene) shows one-dimensional chain, while Cu(2,13-dioxoOEiBC) shows no  $\pi$ - $\pi$  stacking interaction.

### EXPERIMENTAL SECTION

**General Information.** All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Hhfa(hexafluoropentanedione) and H<sub>2</sub>OEP(octaethylporphyrin) were purchased from Aldrich

Chemicals and used as received. UV/Vis/NIR electronic absorption spectra were obtained on a Perkin-Elmer UV/Vis/NIR Lambda 19 spectrophotometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer 883 spectrometer.

**Synthesis of Cu(hfa)<sub>2</sub>( $\mu$ -1,4-dicyanobenzene).** To a benzene solution of Cu(hfa)<sub>2</sub> (0.20 g, 0.42 mmol) was added 1,4-dicyanobenzene (0.054 g, 0.42 mmol). The resulting solution was refluxed for 24 h. After cooling to ambient temperature, the solution was filtered and volume of the filtrate was reduced to half. Slow evaporation of this solution gave green crystals suitable for X-ray crystallography. Yield: 0.22 g, 87%. mp 181-193 °C. IR (KBr, cm<sup>-1</sup>): 3380 (br, m), 2210(m), 1625(s), 1550(m), 1525(m), 1390(m), 1245(s), 1220(s), 1140(s), 1095(m), 842(m), 795(s).

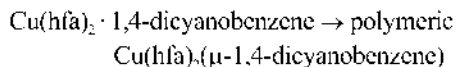
**Synthesis of Cu(2,13-dioxoOEiBC).** Synthesis of H<sub>2</sub>(2,13-dioxoOEiBC), 3,3,7,8,12,12,17,18-octaethyl-(3H,12H)-porphine-2,13-dione, was based on the literature with modification.<sup>11</sup> The crude product was chromatographed into two fractions on a silica gel column (60-200 mesh). The first fraction was collected with dichloromethane/hexane (60:40

volume) until the eluent became green. The second fraction was eluted with dichloromethane. The second fraction was rechromatographed on a silica gel column using dichloromethane/hexane (70:30 volume). The last fraction, containing  $H_2(2,13\text{-dioxoOEiBC})$ , was collected. Yield: 5%. UV-vis(dichloromethane solution):  $\lambda_{\text{max}}$  398, 410, 514, 550, 654, 688 nm. Insertion of copper into the  $H_2(2,13\text{-dioxoOEiBC})$  was accomplished by the reaction of free base and copper(II) acetate in DMF. The reaction product was chromatographed on a silica gel column (60-200 mesh) using dichloromethane/hexane (50:50 volume). Dark violet  $Cu(2,13\text{-dioxoOEiBC})$  was eluted as a major product. UV-Vis(dichloromethane solution):  $\lambda_{\text{max}}$  403(soret), 600, 605 nm. IR(KBr):  $\nu_{\text{C=O}}$  1712  $\text{cm}^{-1}$ .

Oxidation of  $Cu(2,13\text{-dioxoOEiBC})$  was carried out by the reaction of  $Cu(2,13\text{-dioxoOEiBC})$  with tris(4-bromophenyl)ammonium hexachloroantimonate.  $Cu(2,13\text{-dioxoOEiBC})$  (25 mg, 0.040 mmol) and tris(4-bromophenyl)ammonium hexachloroantimonate (34 mg, 0.042 mmol) were placed in a 100 mL Schlenk flask and dried for 1 h. After drying, dichloromethane was added to the Schlenk flask and the solution immediately turned brown. After stirring for 30 minutes, hexane was added to the solution. The mixture was filtered, and the brown solid was dried in vacuo; the yield was quantitative. UV-Vis (dichloromethane solution):  $\lambda_{\text{max}}$  385, 510, 590 nm. IR(KBr):  $\nu_{\text{C=O}}$  1725  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

$Cu(hfa)_2(\mu\text{-}1,4\text{-dicyanobenzene})$  was obtained by the reaction of  $Cu(hfa)_2$  and 1,4-dicyanobenzene in benzene. Suitable crystals were harvested from the slow evaporation of the benzene solution.



The molecular structure of  $Cu(hfa)_2(\mu\text{-}1,4\text{-dicyanobenzene})$  is shown in Fig. 1, with the F atoms of hfa anionic ligands are omitted for clarity.<sup>12</sup>

Copper atom binds to four oxygen atoms, con-

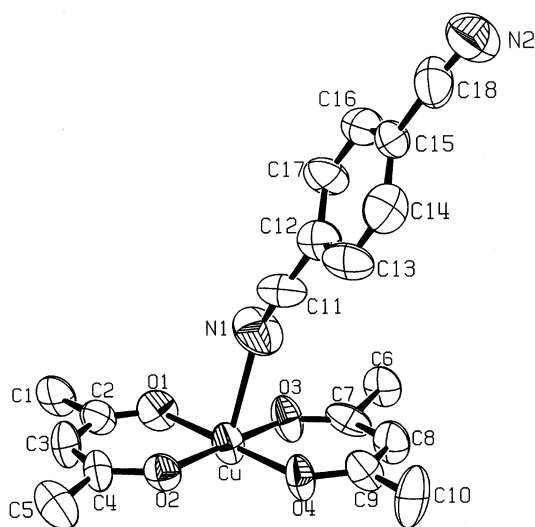


Fig. 1. ORTEP diagram of the crystal structure of  $Cu(hfa)_2(\mu\text{-}1,4\text{-dicyanobenzene})$  showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

tributed by two bidentate hfa anionic ligands, resulting in a square planar structure. The square planar  $Cu(hfa)_2$  unit is bridged by 1,4-dicyanobenzene to give a linear structure. The extended one-dimensional polymeric structure of this compound

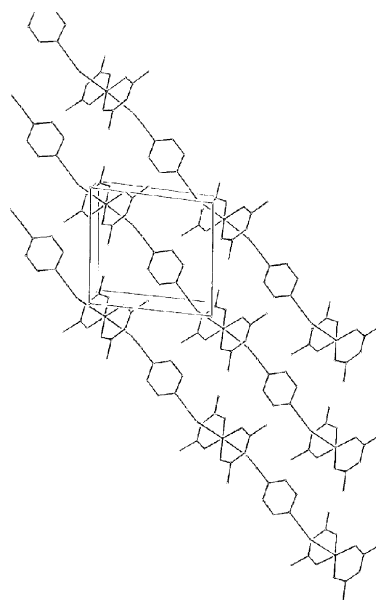


Fig. 2. Unit cell packing diagram of  $Cu(hfa)_2(\mu\text{-}1,4\text{-dicyanobenzene})$  showing one-dimensional chains.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene)

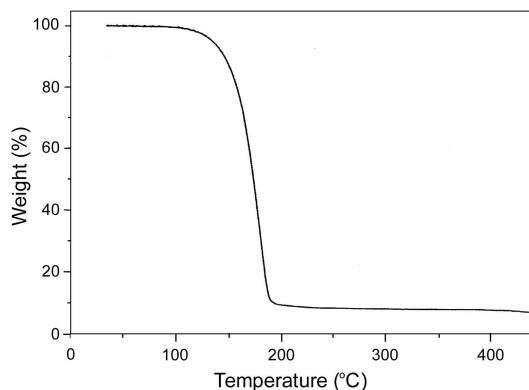
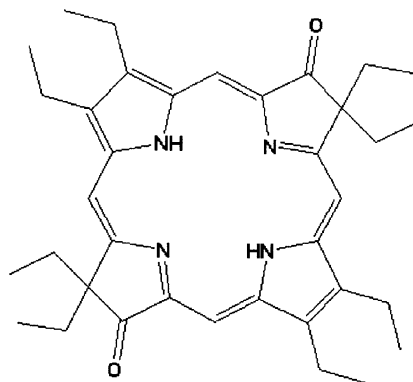
Cu-O(1)	1.980(9)	Cu-O(2)	1.971(8)
Cu-O(3)	1.917(9)	Cu-O(4)	1.906(8)
Cu-N(1)	2.534(9)	Cu-N(2)	2.549(8)
O(1)-C(2)	1.24(2)	O(2)-C(4)	1.254(14)
O(3)-C(7)	1.26(2)	O(4)-C(9)	1.28(2)
C(1)-C(2)	1.61(2)	C(2)-C(3)	1.33(2)
C(3)-C(4)	1.38(2)	C(4)-C(5)	1.50(2)
C(6)-C(7)	1.599(14)	C(7)-C(8)	1.38(2)
C(8)-C(9)	1.44(2)	C(9)-C(10)	1.46(2)
C(11)-N(1)	1.14(2)	C(18)-N(2)	1.14(2)
O(1)-Cu-O(2)	92.7(4)	O(1)-Cu-O(3)	87.0(4)
O(1)-Cu-O(4)	179.0(6)	O(2)-Cu-O(3)	178.8(5)
O(2)-Cu-O(4)	88.0(4)	O(3)-Cu-O(4)	92.3(4)
O(1)-Cu-N(1)	94.5(4)	O(2)-Cu-N(1)	97.3(5)
O(3)-Cu-N(1)	83.8(6)	O(4)-Cu-N(1)	86.0(6)
O(1)-Cu-N(2)	85.8(4)	O(2)-Cu-N(2)	86.4(5)
O(3)-Cu-N(2)	92.4(6)	O(4)-Cu-N(2)	93.6(6)

is depicted in Fig. 2.

The Cu-O bond distances fall into two distinctly different groups; Cu-O(1) and Cu-O(2), 1.975[9] Å and Cu-O(3) and Cu-O(4), 1.912[9] Å. The average Cu-N bond distance is 2.542[9] Å. The average ring O-Cu-O angle is 92.5[4]°. A comparison of bond distances and angles of Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene) with those of other complexes containing Cu(hfa)<sub>2</sub> unit, Cu(hfa)<sub>2</sub> and Cu(hfa)<sub>2</sub>(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH), is shown in Table 2.<sup>13</sup> This reveals that the average Cu-O bond distance of the six-coordinated Cu(hfa)<sub>2</sub>(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH), 1.990[4] Å, is longer than in four-coordinated Cu(hfa)<sub>2</sub> compound, 1.911[7] Å. Interestingly, the molecular structure of Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene) shows two distinct types of Cu-O bond distance, short distance with one hfa ligand and longer distance with the other hfa ligand. The average Cu-

Table 2. Comparison of the Cu-O, Cu-N Bond Lengths (Å) and O-Cu-O Angles (deg)

	Cu-O	Cu-N	O-Cu-O
Cu(hfa) <sub>2</sub>	1.911[7]		93.0(3)
Cu(hfa) <sub>2</sub> (H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH)	1.990[4]	2.003(4)	87.7[2]
Cu(hfa) <sub>2</sub> (μ-1,4-dicyanobenzene)	1.912[9]	2.542[9]	92.5[4]
	1.975[9]		

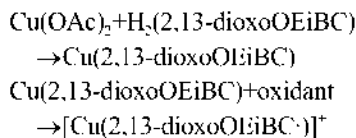
Fig. 3. TGA diagram of Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene).Fig. 4. The structure of H<sub>2</sub>(2,13-dioxoOEiBC).

N distance in Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene), 2.542[9] Å, is longer than in Cu(hfa)<sub>2</sub>(H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH), 2.003(3) Å, indicating a Jahn-Teller elongation along N(1)-Cu-N(2) vector. The thermogravimetric behaviors of the complex have been investigated by thermogravimetry (TGA) over the temperature range 30–450 °C.<sup>14</sup> Atmospheric pressure thermogravimetric analysis of Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene) reveals that weight loss takes place in the 100–190 °C temperature range and shows that no weight loss after 200 °C.

The final residual weight (11%) agrees with the composition of CuO(12%). Cu(hfa)<sub>2</sub> has been used for the chemical vapour deposition(CVD) of copper films.<sup>15</sup> The TGA analysis indicates that Cu(hfa)<sub>2</sub>(μ-1,4-dicyanobenzene) can not be used as a CVD precursor.

Cu(2,13-dioxoOEiBC) was obtained by the reaction of Cu(OAc)<sub>2</sub> and H<sub>2</sub>(2,13-dioxoOEiBC) in DMF.

The oxidation of Cu(2,13-dioxoOEiBC) with tris(4-bromophenyl)aminium hexachloroantimonate results in the formation of the  $\pi$ -cation radical, [Cu(2,13-dioxoOEiBC)]<sup>+</sup>[SbCl<sub>6</sub>]<sup>-</sup>.



The electronic spectra of [Cu(2,13-dioxoOEiBC)]<sup>+</sup> has a blue-shifted and broadened Soret band and the bands in the visible region have decreased in intensity. These spectral changes is characteristics for the formation of the metalloporphyrin  $\pi$ -cation radical. New near-IR bands have been observed in metallooctaethylporphyrin  $\pi$ -cation radicals, where they result from the formation of dimeric  $\pi$ -cation radical species, [M(OEP)]<sub>2</sub><sup>2+</sup>. These near-IR bands are found at 900-960 nm for nickel, copper, palladium, and zinc octaethylporphyrin  $\pi$ -cation radicals.<sup>10</sup> Similarly, the  $\pi$ -cation radical complexes of the metallo-oxooctaethylchlorin show near-IR bands. [Cu(oxoOEC)]<sub>2</sub><sup>2+</sup> has two overlapped near-IR absorption bands at 1285 and 1548 nm.<sup>9</sup> Upon oxidation of Cu(2,13-dioxoOEiBC), however, no near-IR band is observed in the region of 900-3000 nm at the highest concentration we were able to use. This observation suggests that the [Cu(2,13-dioxoOEiBC)]<sup>+</sup> radical is monomeric because the increased number of peripheral substituents prevents aggregation of the molecule. This phenomenon is also found in [Cu(TPP)]<sup>+</sup> and [Cu(TMP)]<sup>+</sup> radicals. The solid-state structures of [Cu(TPP)]<sup>+</sup> and [Cu(TMP)]<sup>+</sup> show no  $\pi$ - $\pi$  aggregation due to the bulky peripheral substituents.<sup>16</sup>

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- Abbreviations used in this paper include: 2,13-dioxoOEiBC, 3,3,7,8,12,12,17,18-octaethyl-(3H,12H)-porphine-2,13-dionato(2-); hfa, anion of hexafluoropentanedione; H<sub>2</sub>OEP,

octaethylporphyrin; H<sub>2</sub>oxoOEC, oxooctaethylchlorin;  
DMF, N,N-dimethylformamide; TMP, dianion of tetrame-

sitylporphyrin; TPP, dianion of tetraphenylporphyrin.